
VI.10 Effect of Coal Contaminants on Solid Oxide Fuel Cell System Performance and Service Life

Objectives

- Determine the sensitivity of solid oxide fuel cell performance to trace level contaminants present in coal-derived gas streams.
- Assess the catastrophic damage risk and long-term cumulative effect of trace level contaminants.
- Assess the life expectancy of solid oxide fuel cell systems fed with coal-derived gas streams.

Accomplishments

- Conducted a critical review of literature which indicated that Ni-cermet-based solid oxide fuel cells (SOFC) are vulnerable to degradation in the presence of contaminants that are expected to be present in a coal-derived fuel gas stream.
- Performed thermodynamic calculations to determine the speciation of various contaminants at SOFC operating temperatures.
- Assembled and tested several Ni-cermet SOFCs under varying conditions with select contaminants in a simulated coal-derived gas stream.

Introduction

SOFCs have high fuel-to-electricity conversion efficiency, environmental compatibility (low NO_x production), and modularity. They operate in the temperature range 600°C-1,000°C and can use fuel streams containing both H_2 and CO . Thus, they are ideal candidates to be integrated with a gas stream

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from an advanced coal gasifier. However, impurities containing virtually every element in the periodic table are present in coal (Clarke and Sloss, 1992) and many become constituents of coal-derived gas. The distribution of trace level contaminants between gaseous and solid phases depends on the individual gasification processes. The contaminants associated with the gaseous phase have deleterious effects on the performance and lifetime of coal-derived gas fed SOFCs.

The well-known impurities in the coal-derived gas stream include H_2S , NH_3 , and HCl vapors; metal impurity species of alkali metals such as Na and K; volatile metals such as Zn, Cd, and Hg; metalloids such as As, Se, and Sb; and transition metals such as Ni, Cr, Mn, and V (Pigeaud and Helble, 1994). The concentrations of the trace elements in coals vary widely from sub-ppm levels to 0.1% depending on the coal rank and location of the deposit. Some of these contaminants such as H_2S are removed by several methods. This program addresses effect of the key impurities such as HCl , methyl chloride, zinc, mercury, arsenic, phosphorous on the efficiency and lifetime of SOFCs.

Approach

The research program includes a literature review, thermodynamic calculations, and a comprehensive experimental and analytical study to assess the impact of trace contaminants on SOFC performance.

1. A review of the scientific literature provided a preliminary assessment of the effect of trace level contaminants on the performance of the SOFC.
2. Thermodynamic equilibrium calculations allow the identification of the chemical nature of the trace contaminants as they pass through the gas cleanup system from the coal gasifier and enter the SOFC anode.
3. A well-defined experimental program is designed to substantiate the preliminary assessment based on thermodynamic calculations and literature data.

In this program, the SOFC anodes (Ni-cermet) are exposed to a simulated coal gas containing individual contaminants at the operating temperature range of the SOFC (800°C to 1,000°C) for an extended period of time. During such exposure, the electrical performance of the SOFC is monitored and compared with another cell that is exposed to a clean simulated coal gas stream to determine the performance degradation. After the exposure period, the anodes are analyzed for the accumulation of the contaminants by the well-known

methods including inductively coupled plasma-atomic emission, and graphite furnace-atomic absorption spectroscopies.

Results

We reviewed the information available in the literature relating to the effect of trace element contaminants on the SOFC performance and nickel reforming catalysts and performed thermodynamic equilibrium calculations to determine the chemical nature and abundance of relevant trace element species as a function of temperature in the range expected in a coal gasification system and SOFC operating conditions.

Of the limited number of investigations that have been conducted to determine the effect of contaminants in the coal-derived gas on the performance of SOFC, H_2S has received most attention followed by NH_3 and HCl vapor (EG & G Technical Services, 2002). At $1,000^\circ\text{C}$, NH_3 , at about 5,000 ppm levels, did not have a measurable effect. HCl at 1 ppm level did not affect the performance of the SOFC either, although higher levels may have a long-term effect. H_2S at 1 ppm level showed an immediate degradation, but then it stabilized with no long-term effect. Higher levels of H_2S and HCl and lower operating temperatures can lead to a significant degradation of SOFC performance (Singhal and Kendall, 2003). Studies of nickel reforming catalysts have also shown that the presence of 1 ppm of As_2O_3 in the feed steam will impair the performance of the reformer in a matter of few days and the effect is irreversible (Twigg, 1996).

We performed thermodynamic equilibrium calculations using gas streams representative of an oxygen-blown slagging gasifier. Based on their abundance in coal, volatility during gasification, and their potential effect on the SOFC performance, the components likely to contribute to degradation when the SOFC anode is operated with coal gas stream are metalloids such as As, Sb, and Se; vaporizable metals such as Zn, Cd, Hg, and Pb; transition metals such as Fe, Cr, and V; and chlorine compounds such as HCl and CH_3Cl . For these calculations, we assumed that the system pressure will be 10 atm and the components will be initially present at 10 ppm level. We calculated the most likely species that will be present at SOFC operating temperatures.

Figure 1 shows a representative thermodynamic calculation performed for arsenic. During coal gasification, arsenic is converted into a hydride, most likely in the form of $\text{AsH}_3(\text{g})$. We calculated the fate of $\text{AsH}_3(\text{g})$ in the gas stream as it is being heated to the SOFC operating temperature and the results are shown in Figure 1. At these temperatures, the predominant species is $\text{As}_2(\text{g})$. Similar to As, Sb is predominantly to be present as $\text{Sb}_2(\text{g})$.

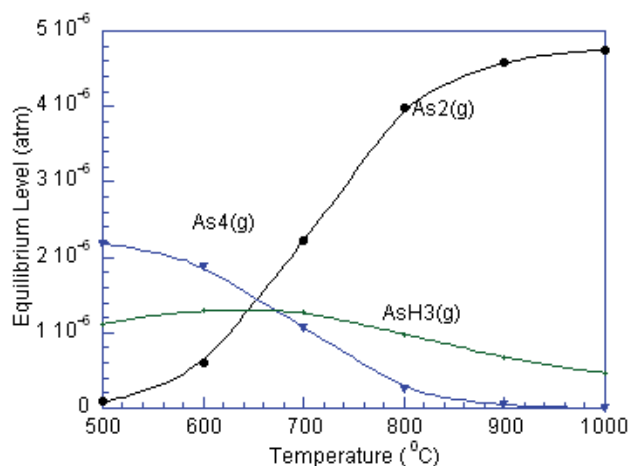


FIGURE 1. The Equilibrium Level of Arsenic Species (Inlet Level 10 ppm) as a Function of Temperature at 10 atm in a Gas Stream Representative of an Oxygen-Blown Slagging Gasifier

The promising sorbent for reducing H_2S level in the coal gas stream at elevated temperatures contains zinc compounds (e.g., zinc titanate or zinc aluminate). In the coal gas streams and HCl levels, zinc can be present as Zn or ZnCl_2 vapors. Similarly, cadmium is likely to be present as $\text{Cd}(\text{g})$ or $\text{CdCl}_2(\text{g})$. Under gasification conditions, Hg is present mainly as $\text{Hg}(\text{g})$. The most likely form of Pb species are $\text{Pb}(\text{g})$, $\text{PbCl}(\text{g})$ and $\text{PbCl}_2(\text{g})$. The actual concentrations of these species will depend on the type of coal used.

$\text{HCl}(\text{g})$ is a known contaminant in the coal derived gas stream and it is thought to be present in the range 10 to 300 ppm. Although the preliminary results indicate that HCl may not be a serious poison at levels of about 1 ppm, $\text{HCl}(\text{g})$ can transport other impurities such as Fe, Cr, Zn, and Pb as volatile chloride species. In desulfurization systems using organic solvents such as monoethyl amine (MEA), HCl can react with the solvent to form CH_3Cl species at low temperatures. Our calculations indicate the trace levels of CH_3Cl will be converted to CH_4 and HCl gases.

In parallel to literature review and thermodynamic calculations, we initiated an experimental program using solid oxide Ni-cermet fuel cell samples from InDec B. V., Netherlands (4.5 cm^2 active area). They have electrolyte layer of dense YSZ of 4 to 6 μm in thickness, porous anode layer of 5 to 10 μm , porous anode support layer of 520 to 600 μm , and a porous LSM-YSZ cathode layer of 30 to 40 μm thick. The cells were operated at 750°C to 850°C with syngas (30% CO , 30.6% H_2 , 11.8% CO and 27.6% H_2O) under 1 A load. The select contaminants (10-50 ppmv) were added to the feed gas stream.

After stabilization in the simulated coal-derived gas mixture without known contaminants, the cell was exposed to a low level of select contaminants

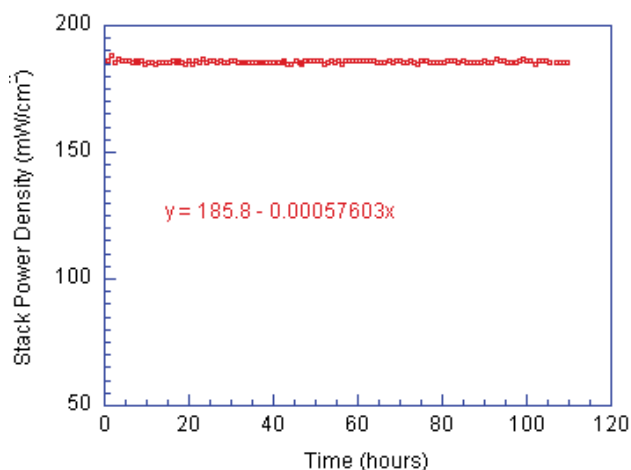


FIGURE 2. The Performance of Cell #6 at 800°C at 1A Load with Simulated Coal-Derived Gas (100 cc/min) Containing Approximately 40 ppm of HCl Vapor

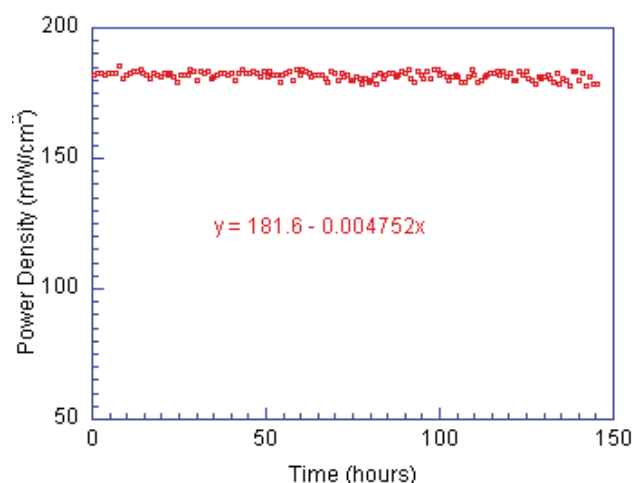


FIGURE 3. The Performance of Cell #7 at 800°C at 1A Load with Simulated Coal-Derived Gas (100 cc/min) Containing Approximately 40 ppm of CH_3Cl vapor.

(10-50 ppmv) by adding them into the simulated gas mixture. Figure 2 shows the performance of this cell (#6) in the gas mixture containing approximately 40 ppm HCl for 100 hours. An examination of the data shows that a gradual performance degradation in the presence of the HCl vapor. In a similar test, we exposed another cell (#7) to approximately 40 ppm CH_3Cl (another potential contaminant in coal-derived fuel gas streams) in the simulated coal-derived gas mixture. Figure 3 shows the exposure testing data of this cell to CH_3Cl during a period of 100 hours.

In the 100-hour test period at 800°C, cell performance was degrading at 0.0006 mW/cm^2 per hour for HCl, and 0.05 mW/cm^2 per hour for CH_3Cl . If the degradation continues, it may be a significant loss over the 30,000-hour expected operating life of the SOFC.

Conclusions and Future Directions

- A review of the available literature indicates that Ni-cermet-based SOFCs are vulnerable to degradation in the presence of contaminants that are expected to be present in a coal derived fuel gas stream. Whereas the effect of some contaminants such as H_2S , NH_3 and HCl has been studied, the effect of other contaminants has not been ascertained.
- The literature relating to the catalytic activity of Ni-based catalysts indicated that many of the potential contaminants could have a deleterious activity of Ni-based SOFCs. S, Cl, P, As, and Bi-containing compounds reduced the chemisorption of H atoms or CO on nickel surfaces leading to a reduction in the catalytic activity that involves H_2 or CO, as would be the case in a SOFC anode.

- A slow degradation of in the power density of the SOFC cell was observed with HCl and CH_3Cl contaminants during the test period of 100 hours at 800°C (0.0006 mW/cm^2 per hour for HCl, and 0.05 mW/cm^2 per hour for CH_3Cl). Experiments are in progress for other test conditions.
- We will expose the SOFC cells to additional contaminants such as PH_3 , AsH_3 , Hg, and Zn in the range of 1 to 10 ppm levels for a minimum of 100 hours at 700°C to 900°C and characterize the changes in the performance of fuel cells by monitoring current-voltage characteristics.

FY 2006 Publications/Presentations

- Effect of Coal Contaminants on Solid Oxide Fuel System Performance and Service Life, Quarterly Technical Progress Report 1 covering the period October 1, 2005 through December 31, 2005.
- Effect of Coal Contaminants on Solid Oxide Fuel System Performance and Service Life, Quarterly Technical Progress Report 2 covering the period January 1, 2006 through March 31, 2006.

References

- Clarke, L. B. and L. L. Sloss (1992). Trace Elements – Emissions from Coal Combustion and Gasification, IEA Coal Research, London.
- EG & G Technical Services (2002). Fuel Cell Handbook, 6th edition, DOR/NETL 2002-1179.
- Pigeaud, A. E., and J. J. Helble (1994). “Trace Species Emissions for IGFC,” Proceedings of the Coal-Fired Power Systems 94 – Advances in IGCC and PFBC Review

Meeting, Eds. H. M. McDaniel, R. H. Staubly, and V. K. Venkataraman, DOE/METC-94/1008.

4. Singhal, S. C. and K. Kendall (2003). High Temperature Solid Oxide Fuel Cells: Fundamentals, Design, and Applications, Elsevier, Oxford, England.

5. Twigg, M. (1996), Catalyst Handbook, 2nd edition, Manson Publishing Ltd, London, England.